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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Cellular or Compact Polyurethanes and/or
Polyurethane-Polyureas, a Process for Their Preparation,
and Their Use

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Cellular or compact polyurethanes and/or polyurethane-p lyureas, a process for their preparation, and their use

A b s t r a c t

Cellular or compact polyurethanes and/or polyurethane-polyureas contain, in integrated form, metal phosphates and/or amine salts of acidic metal phosphates.

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5 Cellular or compact polyurethanes and/or polyurethane-polyureas, a process for their preparation, and their use

When improving the fire behaviour of polyurethane-urea foams, it is increasingly desired to avoid halogen-containing additives.

10 Attempts are therefore being made, for example, positively to affect the fire behaviour of polyurethane or polyurea foams by adding halogen-free inorganic fillers, which may also include metal phosphates.

15 These inexpensive fillers, which are frequently employed in large amounts, are quite effective at reducing the specific fire load, although they are less effective at reducing burning itself. They usually have a highly adverse effect on the mechanical properties of the foams, since they are not integrated into the reaction mechanism, but instead are in the form of more or less "dead" inhomogeneities and potential flaws in the cell-wall structure of the foams, causing embrittlement of this.

20 The concomitant use of phosphorus-containing, soluble and in some cases integratable organophosphorus components in the foam formulation is another way of improving the fire behaviour. However, such components are frequently expensive or potentially toxic, or susceptible to hydrolysis with elimination of phosphoric acids. This flameproofing method is therefore frequently unacceptable.

It has now been found that, surprisingly, it is possible to find polyurethane-polyurea (foam) formulations based on polyols and polyisocyanates in which aqueous solutions

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of metal phosphate/amine salts function as a reaction component which can be integrated into the reaction mechanism.

- 5 Surprisingly, polyurethane or polyurea foams are obtained which contain metal phosphates in integrated form, i.e. incorporated more or less homogeneously into the polymer material, for example the cell walls. When viewed on a microscopic level, the cell walls surprisingly have a glass-clear, single-phase character.

It is furthermore surprising that both foams having low densities and tough, resilient properties and of course also those having brittle and rigid foam properties can be obtained.

- 10 It is furthermore surprising that the highly polar, substantially inorganic metal phosphate/amine salt reaction components are apparently integrated homogeneously into the organic material of the foam structure, and the cell walls, when viewed on a microscopic level, can therefore act as small, clear glass sheets.

- 15 Finally, it is surprising that the enormously high water content introduced through the aqueous solutions does not adversely affect foam formation, but instead lightweight, uniformly fine-pored and stable foam mouldings with a homogeneous appearance can be obtained without the need to use a stoichiometrically sufficient amount of polyisocyanate, i.e. an amount which also binds all the water.

- 20 The polyurethanes and polyurethane-ureas according to the invention, preferably polyurethane-urea foams, are thus characterized in that they contain in integrated form at least one metal phosphate and/or amine salt of an acidic metal phosphate, preferably metal phosphates, preferably in amounts of greater than 25% by weight and preferably in extremely finely divided form, i.e. in a form which is virtually uncharacterizably recognizable visually.

- 25 They are produced according to the invention by adding aqueous solutions of metal phosphonate/amine salts, preferably metal phosphate/amine salts, in particular metal phosphate/alkanolamine complexes, as further component to mixtures of reaction, active

ingredient and additive components from polyurethane foam chemistry which are conventional per se in industry, as used for reaction with polyisocyanates to form foams.

5 The invention relates to cellular or compact polyurethanes and/or polyurethane-polyureas containing, in integrated form, metal phosphates and/or amine salts of acidic metal phosphates.

According to the invention, preference is given to:

- 10 - polyurethane and/or polyurethane-polyureas having densities of between 10 and 500 g/l and integrated solids contents of greater than 25% by weight, preferably 50-70% by weight, of amine salts of acidic metal phosphates in the form of reaction products with isocyanate/polyol mixtures,
- polyurethane and/or polyurethane-polyureas, preferably foams, in integrated form containing phosphates of the metals Mg, Ca, Zn, B, Al, Na and K, individually or as a mixture,
- 15 - polyurethane and/or polyurethane-polyurea foams containing ammonium and/or alkanolamine salts of acidic metal phosphates, and
- polyurethane and/or polyurethane-polyurea foams containing monoethanolamine salts of acidic metal phosphates.

20 The invention also relates to a process for the preparation of the preferably cellular polyurethanes and/or polyurethane-polyureas according to the invention by reaction, known per se, of polyisocyanates with compounds containing at least two reactive hydrogen atoms of molecular weight 62-10 000 and optionally auxiliaries and additives, characterized in that aqueous solutions of amine salts of acidic metal phosphates are added as additional reaction components, and preferably the reaction is carried out at

25 isocyanate characteristic indices of greater than 100 (based on the organic reactive components).

Carboxylic acids and/or fatty acids are preferably also added to the reaction mixture.

Preferred amine salts of acidic metal phosphates are alkanolamine salts in addition to ammonium salts.

5 The compounds containing at least two reactive hydrogen atoms of molecular weight 62-10 000 are preferably alkanolamines and/or alkoxylation products thereof, in particular having OH numbers of between 400 and 600.

During the foam production according to the invention, the expansion process is optionally supported by additional supply of heat.

10 The invention furthermore relates to insulating materials and sandwich constructions containing polyurethanes and/or polyurethane ureas according to the invention.

Preference is given according to the invention to metal phosphates. However, this term is also intended to cover metal phosphonates, for example Al salts of methylphosphonic acid and/or metal salts of other polybasic phosphoric acids, for example pyrophosphoric, oligophosphoric or polyphosphoric acid.

15 Suitable metals in the metal phosphates or in the metal phosphate/amine salts are those from the first, second and third, and eighth group of the Periodic Table, such as, for example, Fe, Ni, Mg, Ca, Ba, Zn, preferably B, Al and optionally Na and K, individually and/or in combination with one another.

20 Preferred metal phosphate/amine salts are those in which the amines used are alkanolamines and/or ammonia, in particular monoethanolamine, but optionally also di- or triethanolamine.

The aqueous metal phosphate/amine salt solutions used according to the invention are preferably aqueous solutions of products of the reaction of alkanolamines with acidic metal phosphates. These are described, for example, in German Offenlegungsschriften
25 3 833 977, 3 912 552, 4 023 310 and 4 126 702, in particular the boron-containing

metal phosphate/amine salts or aqueous amine salt solutions described in German Offenlegungsschriften 4 226 044, 4 236 936, 4 314 299 and 4 339 474, or alternatively the silica sol-containing products described in German Offenlegungsschrift 4 401 636.

5 The simplest form of the preparation of such metal phosphate/amine salt solutions comprises adding an alkanolamine or alkanolamine mixture to an acidic phosphate of one of said metals in aqueous medium with good stirring and optionally warming to from 20 to 120°C while setting pH values of between about 5.5 and 8, preferably between 6 and 7.5.

10 For the use according to the invention as a component in the foam reaction mixture, these solutions expediently have water contents of less than 50% by weight, preferably from 40 to 20% by weight.

15 In the preparation, known per se, of cellular or compact polyurethane-ureas, including foams, polyisocyanates (for example based on diphenylmethane diisocyanate) are reacted with compounds containing at least two reactive hydrogen atoms, generally with molecular weights of from 62 to 10 000, and optionally with active ingredient and additive components, to which the aqueous metal phosphate/amine salt solutions are added according to the invention. The following combinations have proved particularly suitable according to the invention:

20 As compounds containing at least two reactive hydrogen atoms and generally having molecular weights of from 62 to 10 000, alone or as a mixture:

25 In particular aliphatic, preferably tertiary alkoxylation products, in particular ethoxylation and/or propoxylation products of ammonia and/or polyamines containing 2 to 12, preferably 2 to 8, amino groups, which have OH numbers of greater than 50, preferably greater than 350, such as, for example, triethanolamine or tripropanolamine, or the propoxylation or ethoxylation products of triethanolamine, ethylenediamine, polyethylenepolyamines and mixtures thereof; particularly suitable components which may be mentioned here are triethanolamine and propoxylation products thereof having OH numbers of between 300 and 600.

It is of course also possible additionally to use other known reaction components which contain groups which are reactive with isocyanates and which are conventional in industry, for example polyether-polyols with other, for example non-basic, initiators or having other OH numbers, or those containing carboxyl terminal groups, amino
 5 terminal groups, sugar polyols, ester- and polyester-polyols, polyepoxides, polyether or polyester-polyamines.

As active ingredient components, alone or as a mixture:

In addition to the conventional stabilizers which may be present, usually based on polyether-polysiloxane, and in addition to conventional activators based on tert-amines,
 10 which are generally not absolutely necessary in accordance with the invention, or organometallic compounds:

Carboxylic acids, i.e. mono-, but also polycarboxylic acids having 1 to about 150, preferably 1 to 60, carbon atoms, which are preferably liquid at RT, such as, for example, formic acid, acetic acid, (alkyl)phenylacetic acids, preferably liquid, natural
 15 fatty acids, such as, in particular, oleic acid and ricinoleic acid, but also linseed oil fatty acids, isostearic acid, tall oil fatty acid, soya oil fatty acid, fish oil fatty acid, rapeseed oil fatty acid, other natural or alternatively synthetic fatty acids, and the dimer and trimer acids obtainable from such fatty acids.

Of considerable interest with respect to flame retardancy here are also brominated or
 20 chlorinated fatty acids, such as the products of the adduction of bromine onto oleic acid or linseed oil fatty acids.

Although the presence of such fatty acids is not absolutely necessary for the production of the foams according to the invention, their very preferred presence surprisingly results not only in considerable acceleration of the foam formation, but also
 25 considerably easier foam formation with considerably finer pores than would take place without the presence of the fatty acids.

As additive components, alone or as a mixture:

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In addition to conventional mineral or organic/polymeric fillers: hydrocarbons, in particular low-boiling compounds, such as conventional blowing agents, preferably cyclopentane, or other hydrocarbons, furthermore fluorinated hydrocarbons and/or chlorofluorocarbons, and optionally high-boiling products, such as hydrophobicizing
5 paraffin oils and/or paraffin waxes, polyisobutylenes, polyepoxides, epoxy resins, for example glycidyl ethers of bisphenol A, polysiloxanes, polyolefins, polyfluoropolymers, but also optionally halogenated natural fats and oils, for example rapeseed or soya oil, tall oil and castor oil.

However, these additive components also include additionally flame-retardant, liquid or
10 pulverulent additives, for example expandable graphites, expandable mica, silicates, borosilicates, intumescent or alternatively non-intumescent flameproofing additives, such as phosphorus-containing polyols, ammonium phosphate, ammonium polyphosphate, ethylenediamine phosphate, di- or triethanolamine o-phosphate, melamine, melamine phosphate, melamine cyanurate, dicyandiamide, urea, biuret,
15 amides and esters of phosphoric acids, for example tricresyl phosphate, tris(2-chloroethyl) phosphate, but also ammonium chloride, ammonium bromide or halides of amines and metals, for example NaBr or diethylenetriamine hydrobromide or triethanolamine hydrobromide, also additives of ortho-, meta-, pyro- or polyphosphoric acids, optionally in aqueous solution, or of HCl or HBr, and also
20 additives of TiO_2 , Mg hydroxide, Al hydroxide, rock flour, dolomite, chalk and talc.

According to the invention, the reaction, active-ingredient and additive components introduced separately or individually into the mixing and reaction space are usually mixed and reacted with 100-180% by weight, preferably 105-150% by weight, of the stoichiometrically equivalent amounts (deviations of $\pm 25\%$ are entirely usual) of
25 polyisocyanates. Aliphatic, cyclic, araliphatic or aromatic polyisocyanates as per the prior art are suitable in the process. Preference is given to the aromatic polyisocyanates which are usual in industry, for example toluene diisocyanates and known modification products thereof, preferably industrial, high-boiling MDI compounds and products of the modification thereof.

In addition to these components, aqueous solutions of metal phosphate/amine salts are also added, in accordance with the invention, to the reaction mixture. Although the amounts of the aqueous solutions added can of course be as small as desired, from about 50 to 85% strength, preferably from 60 to 80% strength by weight, aqueous solutions of the metal phosphate/amine salts are added in such amounts that the amount of metal phosphate/amine salt solid present in the system as a whole makes up a proportion in the reaction mixture as a whole of greater than 25% by weight, preferably greater than 50% by weight, in particular from 52 to 70% by weight.

Accordingly, the amount of polyisocyanate used from a stoichiometric point of view is also higher, namely greater than 100% by weight of the equivalent amount of polyisocyanate for the conventional formulation constituents - apart from water - for example greater than 105% by weight, preferably from 105 to 180% by weight.

The usual formulations for the production of the foams according to the invention preferably contain, based on the water- and blowing agent-free solid, preferably from 25 to 70% by weight, in particular from 50 to 65% by weight, of metal phosphate/amine salt, 30-75% by weight, preferably 35-55% by weight, of the abovementioned reaction components, and from 0 to 20% by weight, preferably from 1 to 10% by weight, of the carboxylic acids referred to as active-ingredient components, while the additives referred to as additive components are preferably present in amounts of less than 50% by weight in the formulation as a whole, although significantly higher amounts of additive, for example up to 80% by weight, are also possible, for example in the case of expandable graphite.

Since the aqueous metal phosphate/amine salt solutions to be used concomitantly according to the invention in relatively large amounts have a considerable cooling effect on the reaction mixture, the reaction temperature or reaction rate which becomes established is frequently not sufficient for any blowing agent, for example cyclopentane, also used or the resultant CO_2 to cause good expansion. It is therefore expedient additionally to warm the reaction mixture, either during, before or after the various components have been combined. The warming can be effected by microwaves, by alternating fields, by IR radiation or by heating by means of hot gases

or simply by introducing or passing the reaction mixture into/through a heat exchanger or an oven. Oven temperatures of from 30 to 170°C, in particular from 65 to 95°C, have proven highly successful here.

- 5 The reaction products according to the invention can also be prepared without blowing agents, if desired also under superatmospheric pressure, and obtained, for example, in solid (compact) form, but they are preferably obtained as foams.

- 10 The foam production itself can in principle be carried out by the batch or continuous, high-pressure or medium-pressure or low-pressure mixing processes conventional in Pu foam technology by means of nozzle or stirrer mixing heads. It is also possible to use spraying methods, rotational moulding methods or twin-belt production methods, for example for sandwich production between paper webs, or foam moulding methods in open or closed, heated or unheated moulds, without pressure or under pressure.

The foams which can be obtained generally have densities of between 10 and 500 g/l, preferably between 18 and 50 g/l.

- 15 They are used, in particular, as filling foam, and in the insulation and/or fire-protection fields, where the fire resistance or the low fire load of the foams is of particular interest.

- 20 They can also be used for the production of sandwich parts having a wide variety of outer layers, for example paper, or glass or organic woven fabrics, laid fabrics or non-woven fabrics, plastic, wood or metal, for filling cavities, as fixing aids in the building sector, as sound insulation or as absorbents or adsorbents, as abrasives and polishes, as filter or packaging material, and for impact absorption.

In many cases, they have a thermoplastic character and can be machined or treated by thermal methods, embossed or shaped in several dimensions, or cut.

- 25 The process is described in illustrative terms below. The parts and percentages relate to the weight, unless stated otherwise.

Examples

Example 1

5 A 76% strength slurry of $\text{Al}(\text{H}_2\text{PO}_4)_3$ in water is adjusted to pH 7.0 by means of a 76% strength solution of monoethanolamine in water at from 70 to 80°C with vigorous stirring. The mixture is stirred until a clear solution has formed. The solution is cooled to RT.

10 200 parts of this metal phosphate/amine salt solution are mixed with 50 parts of a product of the propoxylation of triethanolamine, having an OH number of 500, and with 25 parts of oleic acid, 10 parts of triethanolamine, 2 parts of a commercially available polyether-polysiloxane-based stabilizer and 10 parts of cyclopentane.

15 170 parts of a commercially available technical-grade MDI (Desmodur® 44 V 20, Bayer AG) are then added to this well-stirred mixture, and the components are mixed vigorously for a few seconds. When the reaction mixture begins to expand, it is transferred into a box mould, in which it expands to form a very fine-pore, tough, rigid foam with a homogeneous appearance. After 10 days, its density is measured at 31 g/l. The foam comprises about 37% of the metal phosphate/amine salt. It has a correspondingly low carbon content and a correspondingly reduced fire load.

After storage for 10 days under water, the foam still floats. It can be used as an insulation material.

20 Example 2

25 A 70% strength solution of equal parts of diethanolamine and monoethanolamine is stirred at RT into a 70% strength aqueous slurry of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ in such an amount that a pH of 7 is produced. The mixture is then stirred for a further 2 hours at 70°C. The resultant, slightly cloudy solution is treated in the same way as the phosphate salt solution in Example 1.

A similar, very fine-pore foam is obtained which can be used as insulating material.

Example 3

2 768 parts of 85% strength o-phosphoric acid are diluted with 660 parts of water.
624 parts of aluminium hydroxide are then added, and the mixture is stirred at 90°C for
5 30 minutes. A clear solution of acidic aluminium phosphate is obtained.

741.6 parts of o-boric acid are then dissolved in 1 600 parts of monoethanolamine with
addition of 24 parts of water at 70°C, giving a clear solution.

The two clear solutions obtained in this way are then combined at about 80°C with
vigorous stirring, giving a clear solution of the ethanolamine salt of boron/aluminium
10 phosphate.

This is about 76% strength and has a density of about 1.6 and a viscosity of about
3 000 mPas at 20°C.

This solution is referred to as AB solution and is employed for the examples below.

The AB solution is employed in the same way as the metal phosphate/amine salt
15 solution from Example 1. In this case too, a similar foam which can be employed for
insulation material purposes is obtained.

Example 4

The AB solution is used to produce a foam analogously to Example 1, but without
addition of oleic acid. The resultant foam has larger pores than that obtained in
20 Example 3, its density is 40 g/l, and it cures only slowly. The curing is accelerated by
placing the box mould containing the rising foam in a circulating-air oven at 90°C.

The resultant foam is cut into strips measuring 5×20×2 cm and treated with a Bunsen flame. Although the foam burns in the flame, it extinguishes when the Bunsen flame is extinguished, and it evolves only little smoke.

Example 5

- 5 150 parts of AB solution are stirred well with 26 parts of a triethanolamine having an OH number of 480 which has been alkoxyated with equal parts of ethylene oxide and propylene oxide, 12 parts of ricinoleic acid, 7.5 parts of triethanolamine, 2 parts of a commercially available, polyether-polysiloxane-based stabilizer and 10 parts of cyclopentane, the mixture is then mixed vigorously with 85 parts of technical-grade
- 10 MDI.

The reaction mixture expands to give a homogeneous, fine-pore foam having a density of 31 g/l. This foam is likewise self-extinguishing after flame treatment. It contains about 47% of solid in the form of the metal phosphate/amine salt and can be used to fill cavities in the building sector.

15 Example 6

- 50 parts of propoxylated triethanolamine having an OH number of about 500 are mixed vigorously with 25 parts of oleic acid, 16 parts of triethanolamine, 4.5 parts of the stabilizer used in Example 5 and 20 parts of cyclopentane and with 400 parts of AB solution and 30 parts of 40% strength aqueous KOH solution, and then mixed with 180
- 20 parts of technical-grade MDI, and vigorous mixing is continued. As soon as the reaction mixture begins to expand, it is transferred into a box mould, which is placed in a circulating-air cabinet at 90°C, in which the expansion process continues and is completed after about 90 seconds.

- A fine-pore, tough foam having a density of about 25 g/l is obtained. This foam
- 25 contains about 54% of metal phosphate/amine salt solid and is self-extinguishing on flame treatment while developing only a small amount of smoke.

- On microscopic investigation, the cell structure proves to be quasi-glass-clear, without evidence of phase separation between the organic and inorganic phases. This result demonstrates the integrated incorporation of about 54% of the metal phosphate/amine salt into the material. These components, to be added according to the invention, do not have the character of fillers, but instead may form a type of organically modified ceramic cell structure.

Example 7

- As Example 6, but using 600 parts of AB solution and 30 parts of cyclopentane. The expanding reaction mixture is kept in a microwave field until an average temperature of the foam forming of about 90°C is reached. The foaming process is complete after about 1.5 minutes. A foam is obtained which has somewhat larger pores, but a homogeneous appearance and a density of about 30 g/l, which makes a surprisingly soft, almost elastic impression.

- In spite of the large metal phosphate/amine salt content of greater than 60%, microscopic investigation again shows only glass-clear cell walls, without evidence of phase separation.

The organic/inorganic structure formed here may be the cause of the non-brittle behaviour of the foams.

Example 8

- A reaction mixture is prepared as in Example 7, but without the addition of cyclopentane, and the mixture is stirred at a temperature up to 35°C until it becomes viscous and difficult to stir. The reaction mixture is then transferred into a completely filled, pressure-tight board mould, in which it is allowed to react to completion for 10 hours at 90°C under a pressure of 100 bar. A virtually clear, solid board of a tough, thermoplastically deformable material is obtained.

Example 9

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A mixture is prepared from 300 parts of AB solution, 50 parts of ethoxylated ethanolamine having an OH number of 440, 10 parts of triethanolamine, 5.5 parts of 85% strength formic acid, 2 parts of stabilizer from Example 6 and 11 parts of cyclopentane. 170 parts of technical-grade MDI are stirred vigorously into this mixture.

- 5 When the reaction mixture begins to expand, it is transferred into a box mould, in which it expands to give a small-pore foam with a homogeneous appearance. At first, this is relatively brittle. Immediately after expansion, it is placed in a circulating-air cabinet at 90°C and conditioned for 30 minutes, giving a tough, rigid foam having a density of 33 g/l with a self-extinguishing character which no longer appears brittle.

10 **Example 10**

The procedure is as in Example 6, but the oleic acid is now replaced by the same amount by weight of oleic acid which has been reacted with one mole of bromine. The foaming proceeds analogously and, on flame treatment, the resultant foam extinguishes immediately the flame is removed.

15 **Example 11**

- 500 parts of AB solution are pre-warmed to 35°C and mixed vigorously in a mixing apparatus with a blend, prepared at 20°C, of 25 parts of propoxylated triethanolamine (OH number 500), 12.5 parts of oleic acid, 40 parts of triethanolamine, 3 parts of a commercially available polyether-polysiloxane-based stabilizer and 30 parts of cyclopentane, and with 170 parts of a technical-grade MDI (Desmodur 44 V 20, Bayer AG).

- 20 The reaction mixture is transferred into a paper box mould and expanded in a weak microwave field, the microwave warming of the reaction mixture ensuring a temperature base of about 40°C in the reacting mixture. A fine-pore foam with a homogeneous appearance and a density of 30 g/l with a self-extinguishing character is obtained. The foam can be regarded as a rigid foam with a certain amount of elasticity.
- 25 When viewed on a microscopic level, it is evident that even about 60% of added metal

phosphate solid is fully integrated into the foam matrix: the cell walls and cell webs have a glass-clear, transparent character. There are no indications of phase separation.

- Such foams can be freed from a residual water content by microwave drying or oven or air drying. They are suitable as core layers for insulation sandwich boards of low fire load.

Example 12

- 300 parts of AB solution, 25 parts of a triethanolamine which has been alkoxylated to an OH number of 420 by means of a mixture of equal parts of ethylene oxide and propylene oxide, and 13 parts of linseed oil fatty acid, 1 part of stabilizer from Example 11, 25 parts of triethanolamine and 25 parts of pentane are stirred vigorously with 45 parts of technical-grade MDI from Example 11 and 45 parts of technical-grade tolylene diisocyanate (Desmodur T 80, Bayer AG), and the mixture is transferred into a cylindrical mould, in which the material expands to give a foam having a homogeneous pore structure and a density of 28 g/l. The foam is self-extinguishing and can be used for insulation purposes. It is also noteworthy here that the pores of the foam appear to be constructed of a single-phase structural material with a glass-clear appearance, i.e. that the metal phosphate complex has been integrated into the structural material.

Example 13

- As Example 12, but 30 parts of an aliphatic paint isocyanate (Desmodur® N, Bayer AG) have been added to the isocyanate mixture. A foam of an analogous type is obtained, but it has a clearly fine-pore character. It can be used for insulation purposes.

Example 14

- The procedure is analogous to Example 6. However, the propoxylated triethanolamine is now replaced by an equal amount by weight of propoxylated triethylenetetramine,

OH number 455. A self-extinguishing, fine-pore foam having a density of 33 g/l is obtained.

Example 15

- 5 400 parts of AB solution, 25 parts of a product of the propoxylation of ethylenediamine, having an OH number of 470, 15 parts of oleic acid, 3 parts of the stabilizer from Example 11 and 30 parts of cyclopentane are mixed well and then stirred vigorously with 130 parts of technical-grade MDI from Example 11. The mixture is then poured into a box mould, and placed in an oven pre-heated to 60°C. A homogeneously fine-pore rigid foam having a density of 34 g/l and self-extinguishing properties is obtained. Such foams are of interest for cavity foam-filling in the building sector.
- 10

Example 16

- 300 parts of AB solution are stirred at 70°C for 1 hour with 76 parts of $(\text{NH}_4)_2\text{HPO}_4$ and 24 parts of water.
- 15 300 parts of the resultant solution of the ammonium-containing complex formed in this way are stirred at room temperature with 25 parts of a propoxylated ethanolamine having an OH number of about 500, and 12 parts of oleic acid, 20 parts of triethanolamine, 2 parts of a conventional polyether-polysiloxane-based stabilizer and 30 parts of cyclopentane.
- 20 110 parts of a commercially available technical-grade MDI (Desmodur® 44 V 20, Bayer AG) are then added with vigorous mixing, and the mixture is allowed to expand in a box mould.

A fine-pore rigid foam with a homogeneous appearance and a density of about 30 g/l is obtained.

Addition of 20 parts of 40% strength NaOH (aqueous solution) to the reaction mixture before addition of the isocyanate gives a comparable foam having a density of 21 g/l.

- 5 In the flame-treatment test, it is found that these foams have even lower tendency to burn and extinguish even quicker on removal of the flame than a similar foam produced in the same way from pure AB solution.

Example 17

The procedure is as in Example 16, but 50 parts of expandable graphite (SO_x/NO_x expandable graphite, commercial product) are added before the reaction with the polyisocyanate.

- 10 The resultant foam having a density of about 33 g/l intumesces on flame treatment and extinguishes immediately on removal of the flame source. This product is of particular interest for the production of cable ducts and other fire barriers in the area of preventive fire protection.

What is claimed is:

1. Polyurethanes and polyurethane-polyureas which contain, in integrated form, at least one phosphate selected from the group consisting of metal phosphates and amine salts of acidic metal phosphates.
- 5 2. Polyurethanes and polyurethane-polyureas of Claim 1, which are in cellular form.
3. Polyurethanes and polyurethane-polyureas of Claim 1, which are in compact form.
- 10 4. Polyurethanes and polyurethane-polyureas of Claim 1, which have densities of between 10 and 500 g/l and solids contents of greater than 25% by weight of amine salts of acidic metal phosphates in the form of reaction products with isocyanate/polyol mixtures.
- 15 5. Polyurethanes and polyurethane-polyureas of Claim 1, which are foams and contain phosphates of the metals Na, K, Mg, Ca, Zn, B and Al, individually or as a mixture.
6. Polyurethanes and polyurethane-polyureas of Claim 1, which are foams and contain as amine salts of acidic metal phosphates at least one salt selected from the group consisting of ammonium and alkanolamine salts.
- 20 7. Polyurethanes and polyurethane-polyureas of Claim 1, which are foams and contain monoethanolamine salts of acidic metal phosphates.
- 25 8. A process for the preparation of the polyurethanes and polyurethane-polyureas of Claim 1 by reaction of polyisocyanates with compounds containing at least two reactive hydrogen atoms and having a molecular weight of from 62 to 10,000, in which process aqueous solutions of amine salts of acidic metal phosphates are added as additional reaction components.

9. The process of Claim 8, in which cellular polyurethanes and polyurethane-polyureas are prepared.
10. The process of Claim 8, in which compact polyurethanes and polyurethane-polyureas are prepared.
- 5 11. The process of Claim 8, in which auxiliaries and additives are added.
12. The process of Claim 8, in which the reaction is carried out at isocyanate characteristic indices of greater than 100 (based on organic reactive components).
- 10 13. The process of Claim 8, in which at least one acid selected from the group consisting of carboxylic acids and fatty acids is additionally added.
14. The process of Claim 8, in which alkanolamine salts are used as amine salts of acidic metal phosphates.
- 15 15. The process of Claim 8, in which alkanolamines are used as compounds containing at least two reactive hydrogen atoms and having a molecular weight of 62 to 10,000.
16. The process of Claim 8, in which alkoxylation products of alkanolamines are used as compounds containing at least two reactive hydrogen atoms and having a molecular weight of 62 to 10,000.
- 20 17. The process of Claim 8, which is carried out with alkanolamines having OH-numbers of between 400 and 600.
18. The process of Claim 8, which is carried out with alkoxylation products of alkanolamines having OH-numbers of between 400 and 600.

19. Moldings, insulating materials and sandwich constructions containing polyurethanes and polyurethane-polyureas of Claim 1.

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SUBSTITUTE
REMPLACEMENT

SECTION is not Present
Cette Section est Absente